

Successive Binding Energies of  $\text{Fe}(\text{CO})_5^+$ 

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The  $\text{Fe}(\text{CO})_n^+$  geometries are optimized using second-order Møller–Plesset (MP2) perturbation theory, the modified coupled-pair functional (MCPF) approach, and density functional theory (DFT). The Becke–Lee–Yang–Parr (BLYP) functional yields very poor results, while a semiempirical exchange–correlation functional works very well.  $\text{Fe}(\text{CO})_5^+$  has a doublet ground state, while  $\text{Fe}(\text{CO})_n^+$  for  $n = 1–3$  have quartet ground states. For  $\text{Fe}(\text{CO})_4^+$  the doublet and quartet states are too close in energy to definitively determine the ground state. The calculations show that the small third CO binding energy is not due to a change in spin state from a quartet for  $\text{Fe}(\text{CO})_2^+$  to a doublet for  $\text{Fe}(\text{CO})_3^+$ , but instead is due to the loss of  $\text{sd}\sigma$  hybridization when the third CO is added. The theoretical successive CO binding energies agree best with the revised values of Distefano.

## I. Introduction

There have been several experimental determinations of the successive CO bond energies of  $\text{Fe}(\text{CO})_5^+$ . Using photoionization yield curves, Distefano<sup>1</sup> determined all five CO binding energies, which are summarized in Table 1. (Note we use  $\text{Fe}^+(\text{F}(3\text{d}^7)) + \text{CO}(\text{X}^+)$  for the asymptote of  $\text{FeCO}^+$ , because the bonding in all systems is derived from the  $3\text{d}^7$  occupation of  $\text{Fe}^+$ , and the use of this asymptote allows for a more even-handed comparison of the successive binding energies.) Unfortunately, the photoionization yield curves of Distefano have a long tail for  $\text{FeCO}^+$  and  $\text{Fe}(\text{CO})_2^+$ , making the determination of the threshold very difficult. Halle, Armentrout, and Beauchamp<sup>2</sup> have reinterpreted the results of Distefano. These revised values are in good agreement with the determination of Norwood *et al.*<sup>3</sup> and that of Schultz, Crellin, and Armentrout<sup>4</sup> (SCA) for the first and second CO binding energies and in reasonable agreement with other values<sup>5,6</sup> for the first CO binding energy. We therefore adopt the revised values in this work. Calculations<sup>7</sup> on  $\text{NiCO}^+$  also yield a CO binding energy much smaller than that determined by Distefano using the photoionization yield curves. However, if a different extrapolation of the yield curves is used, the computed and experimental binding energies are in good agreement. This supports the reinterpretation of Halle, Armentrout, and Beauchamp.

It should be noted that the recent density functional theory (DFT) calculations by Castro, Salahub, and Fournier<sup>8</sup> yield an  $\text{FeCO}^+$  binding energy (corrected to  $\text{Fe}^+(\text{F})$  using the experimental  $^4\text{F}–^6\text{D}$  separation averaged over the  $m_j$  values) of 55.8 kcal/mol that would appear to support the original value of Distefano. This large value computed using DFT is somewhat disconcerting considering the good agreement between DFT, more traditional methods, and experiment for the first CO binding energy in  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  (see ref 9 and references therein). However, Delley, Wrinn, and Lüthi report<sup>10</sup> an average CO binding energy for  $\text{Cr}(\text{CO})_6$ ,  $\text{Fe}(\text{CO})_5$ , and  $\text{Ni}(\text{CO})_4$  that is too large for several functionals.

More recently, Norwood *et al.*<sup>3</sup> determined the successive  $\text{Fe}(\text{CO})_5^+$  bond energies using photoelectron–photoion coincidence and photoionization experiments. Their values are in

reasonable agreement with the revised values of Distefano, with the exception of the  $(\text{CO})_2\text{Fe}^+–\text{CO}$  bond energy, where the result of Norwood *et al.* is 7 kcal/mol larger than that of Distefano. As discussed by SCA, the sum of five CO bond energies determined by Norwood *et al.* is about 7 kcal/mol larger than that deduced from the literature thermochemistry ( $142.2 \pm 1.9$  kcal/mol). The values determined by SCA from collision-induced dissociation (CID) are reasonably consistent with the revised values of Distefano, except for the  $(\text{CO})_4\text{Fe}^+–\text{CO}$  bond energy, where the SCA result is 8 kcal/mol larger.

SCA speculated on the origin of the small third binding energy, relative to both the second and fourth binding energies. They noted that  $\text{Fe}(\text{CO})_5$  is a singlet and therefore concluded that  $\text{Fe}(\text{CO})_5^+$  was probably a doublet state. They further noted that calculations showed<sup>11</sup> that  $\text{FeCO}^+$  and  $\text{FeCO}_2^+$  had quartet ground states. They then speculated that the drop in the third CO binding energy was due to a change in spin between  $\text{Fe}(\text{CO})_2^+$  and  $\text{Fe}(\text{CO})_3^+$ . The fourth binding energy was larger than the third because the third had already paid the cost of the spin flip. That is, they suggested that  $\text{FeCO}^+$  and  $\text{Fe}(\text{CO})_2^+$  are quartets, while  $\text{Fe}(\text{CO})_3^+$ ,  $\text{Fe}(\text{CO})_4^+$ , and  $\text{Fe}(\text{CO})_5^+$  are doublets.

We have found<sup>12</sup> a large reduction in the binding energy of the third water to  $\text{Cu}^+$ .  $\text{Cu}^+$  has a  $1\text{S}(3\text{d}^{10})$  ground state, and therefore the spin of all  $\text{Cu}(\text{H}_2\text{O})_n^+$  systems is the same; thus, a change in spin cannot be responsible for the reduction in the third binding energy. For  $\text{CuH}_2\text{O}^+$  and  $\text{Cu}(\text{H}_2\text{O})_2^+$  the repulsion is significantly reduced by  $\text{sd}\sigma$  hybridization, which reduces the metal charge density along the  $\text{O}–\text{Cu}–\text{O}$  axis. However, for  $\text{Cu}(\text{H}_2\text{O})_3^+$  it is impossible to orient the water molecules so as to reduce the repulsion by  $\text{sd}\sigma$  hybridization. Thus  $\text{Cu}–\text{water}$  repulsion is larger and the binding energy smaller when the third water is added. Since a similar bonding mechanism is expected to be operative in  $\text{Fe}(\text{CO})_n^+$ , the reduction in binding energy cannot *a priori* be attributed to a change in the spin state. However, it must be noted that the fourth binding energy for  $\text{Cu}(\text{H}_2\text{O})_n^+$  is not larger than the third as found for  $\text{Fe}(\text{CO})_n^+$ .

In this work we consider the successive CO binding energies of  $\text{Fe}(\text{CO})_5^+$ . Our goals are to determine the origin of the reduction in the third CO binding energy and help differentiate between the various trends in the experimental CO binding energies. We study this problem using traditional *ab initio* methods and the DFT approach.

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TABLE 1: Summary of Successive Binding Energies<sup>a</sup>

	expt			present work <sup>a</sup>			
	Distefano <sup>b</sup>	Norwood <sup>c</sup>	SCA <sup>d</sup>	MCPF	B3LYP	Est1	Est2
Fe <sup>+</sup> -CO	36.9 ± 2.3 <sup>e</sup>	39.3 ± 2.0	36.6 ± 1.8	28.9	37.0	38.8	38.7
FeCO <sup>+</sup> -CO	40.3 ± 2.3 <sup>f</sup>	41.5 ± 1.6	36.1 ± 1.2	29.0	37.0	38.9	38.7
Fe(CO) <sub>2</sub> <sup>+</sup> -CO	18.7 ± 2.3	25.7 ± 1.4	15.9 ± 1.4	15.0	18.1	19.9	19.8
Fe(CO) <sub>3</sub> <sup>+</sup> -CO	25.4 ± 2.3	25.2 ± 1.1	24.7 ± 1.4	20.0	22.5	24.9	24.2
Fe(CO) <sub>4</sub> <sup>+</sup> -CO	18.2 ± 2.3	17.8 ± 0.9	26.8 ± 0.9	9.8	19.2	19.7	20.9
sum <sup>g</sup>	139.5 ± 5.2	149 ± 3.2	140.0 ± 3.1	102.8	133.8	142.2	142.2

<sup>a</sup> The B3LYP frequencies are used to compute the zero-point energies. <sup>b</sup> The values of Distefano<sup>1</sup> as revised by Halle, Armentrout, and Beauchamp.<sup>2</sup> <sup>c</sup> Norwood, Ali, Flesch, and Ng.<sup>3</sup> <sup>d</sup> Schultz, Crellin, and Armentrout.<sup>4</sup> <sup>e</sup> The original value is 57.6 ± 2.3 kcal/mol. <sup>f</sup> The original value is 19.6 ± 2.3 kcal/mol. <sup>g</sup> On the basis of the available literature thermochemistry, SCA<sup>4</sup> deduced a sum of 142.2 ± 1.9 kcal/mol. <sup>h</sup> The dissociation energy for Fe<sup>+</sup>-CO is computed to Fe<sup>+</sup> 4F(3d<sup>7</sup>).

## II. Methods

The Fe basis set is a [8s4p3d] contraction of the (14s9p5d) primitive set developed by Wachters.<sup>13</sup> The s and p spaces are contracted using contraction number 3, while the d space is contracted (311). To this basis set two diffuse p functions are added; these are the functions optimized by Wachters multiplied by 1.5. A diffuse d function<sup>14</sup> and an f polarization function ( $\alpha = 1.339$ ) are added. The final Fe basis set is of the form (14s11p6d1f)/[8s6p4d1f]. The C and O basis sets are [4s3p] contractions of the (9s5p) primitive set optimized by Huzinaga.<sup>15</sup> A d polarization function is added; the exponents are 0.75 for carbon and 0.85 for oxygen. The s space is contracted (5211). A much larger basis set is used in the FeCO<sup>+</sup> and Fe(CO)<sub>2</sub><sup>+</sup> calibration calculations. The large Fe basis set is the (20s12p9d6f4g)/[(6+1)s(5+1)p4d2f1g] set, which is described in detail in ref 16, and the C and O large basis sets are the augmented correlation consistent polarized valence triple-zeta sets of Dunning and co-workers.<sup>17</sup> Only the pure spherical harmonic components of the basis functions are used in all calculations.

In the DFT calculations we use a hybrid functional of the form

$$(1 - A)E_x^{\text{Slater}} + AE_x^{\text{HF}} + BE_x^{\text{Becke}} + CE_c^{\text{LYP}} + (1 - C)E_c^{\text{VWN}}$$

where  $E_x^{\text{Slater}}$  is the Slater exchange,  $E_x^{\text{HF}}$  is the Hartree-Fock exchange,  $E_x^{\text{Becke}}$  is the exchange functional of Becke,<sup>18</sup>  $E_c^{\text{LYP}}$  is the correlation functional of Lee, Yang, and Parr,<sup>19</sup>  $E_c^{\text{VWN}}$  is the correlation functional of Vosko, Wilk, and Nusair,<sup>20</sup> and A, B, and C are the coefficients determined by Becke<sup>21</sup> using his three-parameter fit to the experimental heats of formation for a different choice of the correlation functional. This modification of the original Becke hybrid functional<sup>21</sup> is described in ref 22. This functional is denoted B3LYP and is used to optimize the geometries and compute the frequencies. The binding energies are computed using this functional as well as that of Becke-Lee-Yang-Parr<sup>18,19</sup> (BLYP) at the B3LYP optimized geometries.

In the remaining calculations, the orbitals are optimized at the self-consistent-field (SCF) level. Correlation is added using second-order Møller-Plesset (MP2) perturbation theory, the modified coupled-pair functional (MCPF) method,<sup>23</sup> and the coupled-cluster singles and doubles approach<sup>24</sup> including a perturbational estimate of the triple excitations<sup>25</sup> [denoted CCSD(T)]. The MP2 and CCSD(T) approaches are based on a spin-unrestricted SCF (or unrestricted Hartree-Fock, UHF) wave function, while the MCPF calculations are based on a spin-restricted SCF wave function. In these calculations only the valence electrons are correlated, that is, the Fe 3d and 4s electrons and the CO (3-5) $\sigma$  and 1 $\pi$  electrons.

TABLE 2: Summary of the Calibration Calculations in kcal/mol<sup>a</sup>

	D <sub>e</sub>					D <sub>0</sub>	
	small basis		big basis			corr	best
	MCPF	CCSD(T)	MCPF	MCPF+R	corr <sup>b</sup>		
Fe <sup>+</sup> -CO	30.4	31.4	33.6	37.0	38.0	36.5	38.5 ± 2
FeCO <sup>+</sup> -CO	31.0	34.5	31.7	33.8	37.3	35.4	37.4 ± 2

<sup>a</sup> The zero-point corrections are taken from the B3LYP calculations. The Fe<sup>+</sup>-CO value is computed with respect to Fe<sup>+</sup> 4F(3d<sup>7</sup>). <sup>b</sup> Computed by adding the difference between the MCPF and CCSD(T) results in the small basis set to the MCPF+R results in the large basis set.

The geometries are fully optimized at the B3LYP and MP2 levels of theory, and the computed frequencies confirm that the stationary points correspond to minima. The only exception is Fe(CO)<sub>5</sub><sup>+</sup>, where the calculation of the MP2 frequencies was prohibitively expensive. At the MCPF level the geometry is optimized with the constraint that the symmetry of the molecule is that determined in the B3LYP (or MP2) calculations. A similar procedure was used for the MP2 calculations on Fe(CO)<sub>5</sub><sup>+</sup>, where the symmetry was fixed at that determined by the B3LYP calculations. In the calibration calculations, the effect of relativity (+R) was included using first-order perturbation theory.<sup>26</sup>

The MCPF calculations were performed using the SEWARD-SWEDEN program system<sup>27,28</sup> while the remaining calculations were performed using Gaussian 92/DFT.<sup>29</sup> The calculations were performed using the NASA Ames Central Computer Facility CRAY C90 or Computational Chemistry IBM RISC System/6000 computers.

## III. Calibration Calculations

A series of calibration calculations were performed for FeCO<sup>+</sup> and Fe(CO)<sub>2</sub><sup>+</sup>, which are summarized in Table 2. (The FeCO<sup>+</sup> calculations were previously reported in ref 16.) The geometries were optimized at the MCPF and CCSD(T) levels using the small basis set. The geometries were very similar. The MCPF and CCSD(T) binding energies for FeCO<sup>+</sup> differed by only 1 kcal/mol, while the difference was larger for the second CO binding energy. Using the MCPF geometry from the small basis set, MCPF calculations were performed using the large basis set. The dissociation energies show the opposite effect that was observed when the correlation treatment was improved; namely, the second binding energy has a small basis set effect while the first has a larger effect. Relativistic effects increase both binding energies, because the CO molecules donate some charge to the Fe 4s orbital. Our corrected value is determined by adding our correlation correction, computed as the difference between the MCPF and CCSD(T) results in small basis set, to the MCPF+R results in the large basis set. We convert these to D<sub>0</sub> values using the B3LYP zero-point energies. We suspect

TABLE 3: Summary of Computed  $D_e$  Values in kcal/mol<sup>a</sup>

	MP2	BLYP	B3LYP	MCPF
$\text{Fe}^+-\text{CO}$	30.8	47.8	38.5	30.5
$\text{FeCO}^+-\text{CO}$	38.3	42.6	39.0	31.0
$\text{Fe}(\text{CO})_2^+-\text{CO}$	19.6	22.0	19.0	15.9
$\text{Fe}(\text{CO})_3^+-\text{CO}$	27.4	28.0	24.2	21.7
$\text{Fe}(\text{CO})_4^+-\text{CO}$	44.3	41.0	23.2	13.8

<sup>a</sup> The dissociation energy for  $\text{Fe}^+-\text{CO}$  is computed to  $\text{Fe}^+ 4\text{F}(3d^7)$ .

that these  $D_0$  values are lower bounds as both improvements in the correlation treatment and basis set increase the binding energies. On the basis of experience,<sup>30</sup> we suspect that our corrected values are at least 2 kcal/mol too small and perhaps as much as 4 kcal/mol too small. Therefore, we obtain our best estimates by adding 2 kcal/mol to our corrected values and assigning an error bar of  $\pm 2$  kcal/mol. The best estimates are in good agreement with experiment.

#### IV. Results and Discussion

Although we can compute very accurate binding energies for the first two CO molecules, this level of theory cannot be easily applied to the larger systems. The remaining calculations were performed using the smaller basis set. The geometries were fully optimized at the B3LYP level for all ions and at the MP2 level for  $\text{Fe}(\text{CO})_n^+$ ,  $n = 1-4$ . In all cases the MP2 and B3LYP methods yield structures with the same symmetry. As described above, the MCPF optimizations for all systems and the MP2 optimization for  $\text{Fe}(\text{CO})_5^+$  were constrained to have the symmetry obtained at the B3LYP level. The results of these calculations are summarized in Tables 3-5, which contain the CO binding energies, the geometries, and harmonic frequencies, respectively.

For  $\text{FeCO}^+$  and  $\text{Fe}(\text{CO})_2^+$  we consider only the  $4\Sigma^-$  and  $4\Sigma_g^-$  states, respectively, as previous work has shown<sup>11</sup> that these are the ground states. For  $\text{Fe}(\text{CO})_3^+$ ,  $\text{Fe}(\text{CO})_4^+$ , and  $\text{Fe}(\text{CO})_5^+$ , we consider both the quartet and doublet states. For  $\text{Fe}(\text{CO})_3^+$  all levels of theory yield a quartet ground state with the doublet state significantly higher in energy. The quartet state has  $C_{3v}$  symmetry, with the three CO molecules bent out of the plane. For  $\text{Fe}(\text{CO})_4^+$  we find that the quartet and doublet states are close in energy. The quartet state has  $T_d$  symmetry, and the doublet has  $D_{4h}$  symmetry. At the MCPF level the quartet state is 10.4 kcal/mol below the doublet, while the B3LYP approach has the doublet state 1.2 kcal/mol below the quartet state without zero-point vibration, but 0.6 kcal/mol above the quartet with zero-point energy. The MCPF calculations are biased in favor of the higher spin state; for example, in  $\text{FeCO}$  the  $5\Sigma^-$  and  $3\Sigma^-$  are virtually degenerate at the MCPF level,<sup>31</sup> while experiment<sup>32</sup> shows that the  $3\Sigma^-$  state is 3.2 kcal/mol below the  $5\Sigma^-$  state. While we have far less experience with the B3LYP approach, the  $3\Sigma^-$  state is computed to be 2.5 kcal/mol below the  $5\Sigma^-$  state of  $\text{FeCO}$ , which suggests that the bias is far smaller for the B3LYP functional. Clearly the quartet and doublet states are close in energy for  $\text{Fe}(\text{CO})_4^+$ . Therefore, we summarize the geometry and vibrational frequencies for both states in Tables 4 and 5. Because the quartet is the lower state in our calculations, we use it in our calculation of the CO binding energies, but the calculations are not of sufficient accuracy to definitively determine the ground state of  $\text{Fe}(\text{CO})_4^+$ . For  $\text{Fe}(\text{CO})_5^+$  all levels of theory find the doublet state to be below the quartet. Because the MCPF calculations are biased toward the quartet state, this shows that the ground state of  $\text{Fe}(\text{CO})_5^+$  is a doublet.

We first discuss the nature of the bonding in each system. Regardless of the spin state or the number of CO molecules,

TABLE 4: Computed Geometrically Parameters (Bond Lengths in Å and Angles in deg)

FeCO <sup>+</sup> , C <sub>∞v</sub> Symmetry, <sup>4</sup> Σ <sup>-</sup>								
r <sub>e</sub> (Fe-C)			r <sub>e</sub> (C-O) <sup>a</sup>					
MP2	B3LYP	MCPF	MP2	B3LYP	MCPF			
1.880	1.887	1.922	1.145	1.129	1.136			
Fe(CO) <sub>2</sub> <sup>+</sup> , D <sub>∞h</sub> Symmetry, <sup>4</sup> Σ <sub>g</sub> <sup>-</sup>								
r <sub>e</sub> (Fe-C)			r <sub>e</sub> (C-O) <sup>a</sup>					
MP2	B3LYP	MOPF	MP2	B3LYP	MCPF			
1.936	1.953	1.983	1.143	1.126	1.132			
Fe(CO) <sub>3</sub> <sup>+</sup> , C <sub>3v</sub> Symmetry, <sup>b</sup> <sup>4</sup> A <sub>2</sub>								
r <sub>e</sub> (Fe-C)			r <sub>e</sub> (C-O)			bend out-of-plane		
MP2	B3LYP	MCPF	MP2	B3LYP	MCPF	MP2	B3LYP	MCPF
2.005	2.022	2.051	1.143	1.126	1.132	12.9	12.9	13.3
Fe(CO) <sub>4</sub> <sup>+</sup> , T <sub>d</sub> Symmetry, <sup>4</sup> A <sub>1</sub>								
r <sub>e</sub> (Fe-C)			r <sub>e</sub> (C-O)					
MP2	B3LYP	MCPF	MP2	B3LYP	MCPF			
2.002	2.035	2.061	1.143	1.126	1.132			
Fe(CO) <sub>4</sub> <sup>+</sup> , D <sub>4h</sub> Symmetry, <sup>2</sup> A <sub>1g</sub>								
r <sub>e</sub> (Fe-C)			r <sub>e</sub> (C-O)					
MP2	B3LYP	MCPF	MP2	B3LYP	MCPF			
	1.905	1.926		1.128	1.135			
Fe(CO) <sub>5</sub> <sup>+</sup> , C <sub>4v</sub> Symmetry, <sup>b</sup> <sup>2</sup> A <sub>1</sub>								
r <sub>e</sub> (Fe-C <sub>ax</sub> )			r <sub>e</sub> (C-O <sub>ax</sub> )			r <sub>e</sub> (Fe-C <sub>eq</sub> )		
MP2	B3LYP	MCPF	MP2	B3LYP	MCPF	MP2	B3LYP	MCPF
1.783	1.951	1.990	1.152	1.129	1.137	1.777	1.900	1.917
r <sub>e</sub> (C-O <sub>eq</sub> )			∠C <sub>ax</sub> FeC <sub>eq</sub>					
MP2	B3LYP	MCPF	MP2	B3LYP	MCPF			
1.150	1.129	1.134	97.0	96.3	96.6			

<sup>a</sup> For comparison the bond length of free CO is 1.146, 1.130, and 1.143 Å at the MP2, B3LYP, and MCPF levels of theory, respectively.

<sup>b</sup> The  $\text{Fe}-\text{C}-\text{O}$  angles are  $180^\circ$ .

the bonding is derived from the  $3d^7$  occupation of  $\text{Fe}^+$ . For  $\text{FeCO}^+$  the ground state is  $4\Sigma^-$  with an  $\text{Fe}^+$  occupation of  $3d\sigma^1-3d\pi^43d\delta^2$ . This occupation minimizes the  $\text{Fe}-\text{CO}$  repulsion and maximizes the  $\text{Fe } 3d\pi$  to  $\text{CO } 2\pi^*$  donation. The repulsion in the  $\sigma$  space is further reduced by  $sd\sigma$  hybridization. The CO bond length is shorter than in free CO despite the metal to  $\text{CO } 2\pi^*$  donation as the result of the electrostatic contribution to the bonding. That is, some  $\text{CO}^+$  character mixes into the wave function, and since  $\text{CO}^+$  has a shorter bond length than CO, the CO bond in  $\text{FeCO}^+$  actually contracts relative to free CO.

The bonding in  $\text{Fe}(\text{CO})_2^+$  is similar to that in  $\text{Fe}(\text{CO})^+$ , with the second CO on the opposite side as the first so that they can both benefit from the reduced repulsion due to the  $sd\sigma$  hybridization, which reduces the charge density on both sides of the Fe. Excluding the BLYP results, we find the second CO to be more strongly bound than the first as the cost of the hybridization is shared by the two ligands. The MP2 approach appears to overestimate dramatically this effect.

When the third CO is added, the  $sd\sigma$  hybridization is lost, and there is a significant drop in the binding energy at all levels of theory. Because the  $sd\sigma$  hybridization is lost for all three ligands, the third ligand appears to be very weakly bound. This large reduction in the third ligand binding energy was also found for  $\text{Cu}(\text{H}_2\text{O})_n^+$ , and the decrease in binding energy when the third CO is added is similar to that found for adding the third  $\text{H}_2\text{O}$ . These computed binding energies show that there is no need to invoke a change in the spin to explain the reduction in

TABLE 5: Computed Harmonic Frequencies in  $\text{cm}^{-1}$ 

mode	MP2	B3LYP	mode	MP2	B3LYP
<b>FeCO<sup>+</sup>, C<sub>∞v</sub> Symmetry, <sup>4</sup>Σ<sup>-</sup></b>					
bend	321	319	Fe-C	405	423
C-O <sup>a</sup>	2153	2225			
<b>Fe(CO)<sub>2</sub><sup>+</sup>, D<sub>∞h</sub> Symmetry, <sup>4</sup>Σ<sub>g</sub><sup>-</sup></b>					
bend (π <sub>u</sub> )	81	81	bend (π <sub>g</sub> )	301	289
Fe-C (σ <sub>g</sub> )	341	348	Fe-C (σ <sub>u</sub> )	353	400
bend (π <sub>u</sub> )	439	441	C-O (σ <sub>u</sub> )	2107	2217
C-O (σ <sub>g</sub> )	2158	2268			
<b>Fe(CO)<sub>3</sub><sup>+</sup>, C<sub>3v</sub> Symmetry, <sup>4</sup>A<sub>2</sub></b>					
bend (e)	62	61	bend (a <sub>1</sub> )	74	71
twist (e)	265	255	rock (a <sub>2</sub> )	274	276
Fe-C (a <sub>1</sub> )	284	293	Fe-C (e)	284	306
wag (e)	362	354	wag (a <sub>1</sub> )	378	372
C-O (e)	2088	2222	C-O (a <sub>1</sub> )	2127	2267
<b>Fe(CO)<sub>4</sub><sup>+</sup>, T<sub>d</sub> Symmetry, <sup>4</sup>A<sub>1</sub></b>					
bend (e)	59	55	bend (t <sub>2</sub> )	75	73
twist (t <sub>1</sub> )	269	258	Fe-C (a <sub>1</sub> )	269	275
Fe-C (t <sub>2</sub> )	295	304	wag (e)	372	351
wag (t <sub>2</sub> )	396	377	C-O (t <sub>2</sub> )	2089	2226
C-O (a <sub>1</sub> )	2125	2269			
<b>Fe(CO)<sub>4</sub><sup>+</sup>, D<sub>4h</sub> Symmetry, <sup>2</sup>A<sub>1g</sub></b>					
bend (twist) (b <sub>2u</sub> )	49		bend (scissor) (b <sub>2g</sub> )		95
bend (e <sub>u</sub> )	96		bend (a <sub>2u</sub> )		102
twist (e <sub>g</sub> )	315		rock (a <sub>2g</sub> )		335
Fe-C (a <sub>1g</sub> )	348		Fe-C (b <sub>1g</sub> )		357
Fe-C (e <sub>u</sub> )	386		twist (b <sub>2u</sub> )		443
wag (b <sub>2g</sub> )	540		wag (a <sub>2u</sub> )		546
wag (e <sub>u</sub> )	584		C-O (e <sub>u</sub> )		2201
C-O (b <sub>1g</sub> )	2219		C-O (a <sub>1g</sub> )		2262
<b>Fe(CO)<sub>5</sub><sup>+</sup>, C<sub>4v</sub> Symmetry, <sup>2</sup>A<sub>1</sub></b>					
bend (b <sub>2</sub> )	48		bend (e)		78
bend (b <sub>1</sub> )	96		bend (e)		101
bend (a <sub>1</sub> )	108		wag (e)		312
Fe-C (a <sub>1</sub> )	316		wag (a <sub>2</sub> )		335
Fe-C (b <sub>2</sub> )	340		Fe-C (a <sub>1</sub> )		357
Fe-C (e)	385		wag (b <sub>2</sub> )		416
wag (e)	465		wag (b <sub>1</sub> )		533
wag (a <sub>1</sub> )	568		wag (e)		584
C-O (e)	2201		C-O (a <sub>1</sub> )		2206
C-O (b <sub>2</sub> )	2215		C-O (a <sub>1</sub> )		2258

<sup>a</sup> For comparison the harmonic frequency for free CO is 2110 and 2213  $\text{cm}^{-1}$  at the MP2 and B3LYP levels of theory, respectively.

the third CO binding energy. The optimal structure has C<sub>3v</sub> symmetry, where the CO molecules have bent about 13° out of the plane. While a D<sub>3h</sub> structure would minimize the ligand-ligand repulsion, bending of the CO out of the plane allows some polarization of the Fe which reduces the Fe-CO repulsion. The three singly occupied 3d orbitals are of a<sub>1</sub> and e symmetry, which results in a <sup>4</sup>A<sub>2</sub> state. These open-shell orbitals are of the same symmetry as the CO 5σ orbitals, and therefore this occupation minimizes the Fe-CO repulsion.

Adding the fourth CO results in a <sup>4</sup>A<sub>1</sub> state with T<sub>d</sub> symmetry. Apparently with four CO molecules, any distortion to allow the Fe to polarize increases the ligand-ligand repulsion more than it decreases the Fe-CO repulsion. The three singly occupied 3d orbitals have t<sub>2</sub> symmetry, which again is in the same symmetry as the CO 5σ orbitals. The Fe-C bond length is very similar to that in Fe(CO)<sub>3</sub><sup>+</sup> because the bonding is very similar. While the average CO binding energy decreases when the fourth CO is added, the fourth binding energy is larger than the third. This arises because adding a fourth CO does not cause any changes in Fe-CO interaction, there is only a small increase in the ligand-ligand repulsion, and the loss of sδ hybridization is shared by four CO molecules.

In the doublet state of Fe(CO)<sub>4</sub><sup>+</sup> the 3d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital is empty, where the four CO molecules are along the x and y axes. This

minimizes the Fe-CO repulsion. The 3d<sub>xy</sub>, 3d<sub>xz</sub>, and 3d<sub>yz</sub> orbitals are all doubly occupied to maximize the Fe to CO 2π\* donation. The 3d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital is singly occupied as this orbital is of the wrong symmetry to donate to the 2π\* orbitals.

The optimal Fe(CO)<sub>5</sub><sup>+</sup> structure is a square pyramid. Assume the apex CO is along the z axis and the four equatorial CO molecules are along the x and y axes. For this orientation, the 3d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital is empty and the 3d<sub>2z<sup>2</sup>-x<sup>2</sup>-y<sup>2</sup></sub> orbital is singly occupied. As for the other systems, this minimizes the CO 5σ-Fe repulsion. This is a significant reorganization from the trigonal bipyramid of Fe(CO)<sub>5</sub> where the 3d<sub>2z<sup>2</sup>-x<sup>2</sup>-y<sup>2</sup></sub> orbital is empty to minimize the Fe-axial CO repulsion. We should note that we did attempt to optimize a distorted trigonal bipyramid, but this has an imaginary frequency and collapses to the square pyramid at the B3LYP level. At the MCPF and MP2 levels we optimized the distorted trigonal bipyramid, and it is above the square pyramid. In the distorted trigonal bipyramid the 3dσ orbital is empty to minimize the repulsion between the Fe and the two axial CO molecules, and the b<sub>1</sub> orbital is singly occupied to reduce the repulsion with the equatorial CO molecules. Rearranging to the square pyramid reduces the Fe-CO repulsion, because the empty orbital reduces the repulsion of four CO molecules instead of two.

The computed binding energies are summarized in Table 3. The MP2 and BLYP approaches obtain an unreasonable difference between the first and second CO binding energies when compared with the calibration calculations or with experiment. The B3LYP and MCPF both show a small increase for the second CO, but the B3LYP results are in much better agreement with the calibration calculations and experiment. Clearly, the basis set requirements for the DFT are less severe than for the more traditional approaches. We should also note that our BLYP first CO binding energy is too large as was found by Castro, Salahub, and Fournier,<sup>8</sup> but the BLYP functional leads to less overbinding than that used by Castro, Salahub, and Fournier. A too large CO binding energy, using the BLYP functional as well as for other functionals, was also reported by Delley, Wrinn, and Lüthi.<sup>10</sup> Thus, we conclude that the CO binding energies in the MCO systems are a good test of the accuracy of the functionals. The B3LYP and MCPF yield a fifth CO binding energy that is smaller than the fourth. The difference is much smaller for the B3LYP than the MCPF. The MCPF result is expected to be too small due to the bias against the lower spin state of Fe(CO)<sub>5</sub><sup>+</sup>. Thus, the B3LYP results are expected to be more accurate. The MP2 and BLYP approaches yield a very large increase in the fifth binding energy relative to the fourth. In light of the MCPF, B3LYP, and experimental results, we feel that this indicates a problem with the MP2 and BLYP. For the MP2, the Fe(CO)<sub>5</sub><sup>+</sup> doublet state is not as well described by a single reference as the quartet state of the other systems. This probably leads to the overestimation of the fifth CO binding energy. Apparently due to limitations in the functional, the BLYP method suffers from similar problems.

Excluding Fe(CO)<sub>5</sub><sup>+</sup>, the MP2, B3LYP, and MCPF geometries are in good agreement. For Fe(CO)<sub>5</sub><sup>+</sup> the B3LYP and MCPF agreement is as good as for the other systems, but the MP2 yields Fe-C distances that are too short, consistent with the overestimation of the binding energy. The MP2 and B3LYP vibrational frequencies are in good agreement. The biggest difference is found for the CO stretching frequencies, but this difference is found for free CO, where the MP2 yields a significantly smaller frequency. As a result, the zero-point contribution to the binding energies is very similar at the MP2 and B3LYP levels of theory.

On the basis of the computed binding energies, we do not consider MP2 or BLYP results further, and we focus only on the B3LYP and MCPF results. We use the B3LYP frequencies to compute the zero-point contribution to the binding energies. These  $D_0$  values are summarized in Table 1 along with experiment. The errors in the MCPF results are expected to be larger for the first, second, and fifth CO binding energies. The larger error in the first two arise because the MCPF tends to underestimate the effect of  $sd\sigma$  hybridization, while the fifth CO is underestimated because it is of lower spin than the other systems, as noted above for the  $\text{FeCO}$ . If we assume that the error in these three binding energies is twice as large as that in the third and fourth CO binding energies, we can correct the CO binding energies using the total binding energy deduced by SCA. This leads to the binding energies listed under "Est1" in Table 1. We note that this partitioning of the error leads to first and second CO binding energies that are in good agreement with our calibration calculations. Because there is far less experience with the B3LYP functional, it is more difficult to assign the errors. As the sum of all five binding energies for the B3LYP is in good agreement with experiment and the B3LYP appears to give a more even-handed treatment of different bonding mechanisms, we divide the error equally between all five CO binding energies. These results are labeled "Est2" in Table 1.

The Est1 and Est2 results are in excellent agreement with each other and in good agreement with the experimental results. The average absolute differences between the Est2 result and experiment are 1.7, 2.7, and 3.0 kcal/mol for the results of Distefano, Norwood *et al.*, and SCA, respectively. The calculations strongly suggest that the fifth CO binding energy is several kcal/mol smaller than the fourth as found by Distefano and Norwood *et al.* The calculations confirm that the third CO binding energy is significantly smaller than the first, second, and fourth binding energies but suggest that the value of SCA is too small and the value of Norwood *et al.* is too large. In fact, the calculations suggest that most of the error in the total CO bonding energy of Norwood *et al.* arises from an overestimation of the third CO binding energy.

We have recently suggested<sup>16,33</sup> that the MP2 method is an excellent approach to optimize the geometry and compute the vibrational frequencies for systems containing first transition row atoms. The energetics would then be improved using higher levels of theory. On the basis of these results, it appears that the B3LYP approach is significantly better than the MP2; the B3LYP calculations require less CPU time, memory, and disk space, while giving superior results. In fact, results for the successive CO binding energies of  $\text{Fe}(\text{CO})_5^+$  are superior to the MCPF calculations in the small basis set. Thus, the B3LYP approach might be the method of choice for all but the most accurate calculations on small systems containing transition metals. However, significantly more examples will be required before the accuracy of the method will be established. It is also important to note that this conclusion does not all apply equally to all DFT approaches; the BLYP results were clearly inferior to the B3LYP results or the corrected MCPF results.

## V. Conclusions

We have optimized geometries and computed the harmonic frequencies for the  $\text{Fe}(\text{CO})_n^+$  ( $n = 1-5$ ) systems. We find a quartet ground state for  $n = 1-3$  and a doublet for  $n = 5$ . For  $n = 4$  the quartet and doublet states are too close in energy for a definitive determination of the ground state.

Our best estimates for the CO binding energies determined using the MCPF and B3LYP approaches are in excellent

agreement. Our results are also in good agreement with experiment. The computed results are in best agreement with the revised values of Distefano. Our calculations clearly show that the large reduction in the third CO binding energy arises because of loss of  $sd\sigma$  hybridization, not because of a change in spin state. The results of the calculations strongly suggest that the third CO binding energy of SCA is too small and their fifth CO binding energy is too large and that most of the error in the total CO binding energy of Norwood *et al.* is a result of their third CO binding energy which is clearly too large.

The B3LYP appears to be a better approach than the MP2 for the calculation of geometries and vibrational frequencies of systems containing transition metals. The energetics of the B3LYP approach are better than those at the MCPF level using the same basis set, suggesting that the B3LYP might be the method of choice for all but highly accurate calculations on small systems containing transition metals. However, this must be confirmed by other studies.

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